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FORM PTO-1390 (REV. 5-93) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER 10191/1438
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371	U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 09/555777

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE(S) CLAIMED
PCT/DE99/03155	(01.10.99) 01 October 1999	(02.10.98) 02 October 1998

TITLE OF INVENTION
METHOD FOR FABRICATING COMPOSITE MATERIALS AND REPRESENTATIVES OF SUCH COMPOSITE MATERIALS

APPLICANT(S) FOR DO/EO/US

KNOLL, Guenter; LINDEMANN, Gert; LINDNER, Friederike; WIEDMAIER, Matthias

Applicant(s) herewith submit to the United States Designated/Elected Office (DO/EO/US) the following items and other information

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) immediately rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☐ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☒ has been transmitted by the International Bureau
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)) (unsigned).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
    ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information: International Search Report and Form PCT/RO/101.

Express Mail No. EM360466549US.

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U.S. APPLICATION NO. (if known, see 37 C.F.R. 1.5)	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
09/555777	PCT/DE99/03155	10191/1438

17. ☒ The following fees are submitted:

Basic National Fee (37 CFR 1.492(a)(1)-(5)):
Search Report has been prepared by the EPO or JPO $840.00

International preliminary examination fee paid to USPTO (37 CFR 1.482) $670.00

No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) $690.00

Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO $970.00

International preliminary examination fee paid to USPTO (37 CFR 1 482) and all claims satisfied provisions of PCT Article 33(2)-(4) $96.00

				CALCULATIONS	PTO USE ONLY
ENTER APPROPRIATE BASIC FEE AMOUNT =				$ 840	
Surcharge of $130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1 492(e)).				$	
Claims	Number Filed	Number Extra	Rate		
Total Claims	27 - 20 =	7	X $18.00	$ 126	
Independent Claims	2 - 3 =	0	X $78.00	$ 0	
Multiple dependent claim(s) (if applicable)			+ $260.00	$ 0	
TOTAL OF ABOVE CALCULATIONS =				$ 966	
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				$	
SUBTOTAL =				$ 966	
Processing fee of $130.00 for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +				$	
TOTAL NATIONAL FEE =				$ 966	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). $40.00 per property +				$	
TOTAL FEES ENCLOSED =				$ 966	
				Amount to be: refunded	$
				charged	$

a. ☐ A check in the amount of $__________ to cover the above fees is enclosed.

b. ☒ Please charge my Deposit Account No. 11-0600 in the amount of $966.00 to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 11-0600 A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

By [signature] Reg. No 35,952

[signature]
SIGNATURE

Kenyon & Kenyon
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Richard L. Mayer, Reg. No. 22,490
NAME

6/2/00
DATE

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[10191/1438]

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s)	:	Guenter KNOLL et al.
Serial No.	:	To Be Assigned
Filed	:	Herewith
For	:	METHOD FOR FABRICATING COMPOSITE MATERIALS AND REPRESENTATIVES OF SUCH COMPOSITE MATERIALS
Art Unit	:	To Be Assigned
Examiner	:	To Be Assigned

Assistant Commissioner
for Patents
Washington, D.C. 20231

PRELIMINARY AMENDMENT

SIR:

Please amend the above-identified application before examination, as set forth below.

IN THE SPECIFICATION:

Page 1, delete line 1.

Page 1, before line 3, insert:
--FIELD OF THE INVENTION--.

Page 1, before line 8, insert:
--BACKGROUND INFORMATION--.

Page 1, line 8, change "Composite" to --There are composite--.

Page 1, line 9, delete "are generally known".

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Page 1, delete lines 10 to 12, and insert --hot pressing (unconfined sintering under pressure) is discussed in German Published Patent Application Nos. 37 34 274 and 36 06 403, in which the parent substance contains $Si_3 N_4$ and the metal silicide $MoSi_2$, and in European Patent Application No. 0 335 382, in which the parent substance contains $Si_3 N_4$ and $MO_5 Si_3$ as the metal silicide--.

Page 1, line 13, change "containing" to --contains--.

Page 1, line 15, change "The" to --It is believed that the--.

Page 1, line 16, change ". The" to --, and that the--.

Page 1, delete line 20, and insert --German Published Patent Application No. 195 00 832, i.e., European Patent Application No. 0 721 925, discusses the--.

Page 1, line 24, change "are preferably" to --may be--.

Page 2, delete line 3.

Page 2, before line 5, insert:
--SUMMARY OF THE INVENTION--.

Page 2, line 5, change "The object of" to --An object of an exemplary embodiment of--.

Page 2, delete line 11, and insert --In an exemplary method, where $Me_5 Si_3$ is--.

Page 2, line 18, change "The inventors discovered a way to" to --To--.

Page 2, line 20, change "properties. They" to --properties, it was--.

Page 2, line 22, change "they found" to --it was found that there is--.

Page 2, delete line 24, and insert --finished composite material. In this manner, composite materials were fabricated--.

Page 2, line 27, change "method" to --exemplary method--.

Page 2, line 29, change "exhibit" to --are believed to--.

Page 2, line 31, change "It is not critical when the" to --The--.

Page 3, delete lines 3 to 18, and insert:

--BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows in a diagram, with respect to a sintering temperature, the logarithm of the lower and upper limit values of the N_2 partial pressures, applicable in the method of the exemplary embodiment according to the present invention, for fabricating a composite material containing Mo_5Si_3.

Figure 2 shows in another diagram, with respect to the sintering temperature, the logarithm of the lower and upper limit values of the N_2 partial pressures, applicable in the method of the exemplary embodiment according to the present invention, for fabricating a composite material containing Nb_5Si_3.--.

Page 3, before line 20, insert:

--DETAILED DESCRIPTION--.

Page 3, line 21, change ", in fact," to --believed to be--.

Page 3, line 22, change "may" to --suitably appropriate--.

Page 3, line 25, change "- in" to --(in--.

Page 3, line 26, change "- preferably -" to --, which may be done--.

Page 4, line 4, change “preferably” to --which may occur, for example,--.

Page 4, line 5, change “and preferably” to --including--.

Page 5, line 1, change “with the” to --with the exemplary embodiment of the method of the--.

Page 5, line 13, change “is preferably” to --may be--.

Page 5, lines 14 and 15, change “quite preferably” to --including--.

Page 5, line 19, change “system” to --table or system--.

Page 5, line 22, change “method” to --exemplary embodiment of the method--.

Page 6, line 11, change “Besides” to --Besides the fact--.

IN THE ABSTRACT:

Delete lines 1 to 14, and insert:

-- ABSTRACT OF THE DISCLOSURE

A method for manufacturing composite materials from a parent substance containing silicon nitride and metal silicide, having fixed electrical properties. The molded articles are made, virtually with their final contours, prior to a sintering operation. The parent substance containing Si_3N_4 and a metal silicide is subjected to a gas pressure sintering in a nitrogenous atmosphere. The metal silicide is of the form Me_5Si_3, where Me is a metal. As a function of a sintering temperature, a lower limit of partial nitrogen pressures is selected so that Si_3N_4 is stable at the lower limit and an upper limit of the partial nitrogen pressures is selected so that Me_5Si_3 is stable at the upper limit. The resulting composite material is a silicon-containing composite material made of Si_3N_4 and the metal silicide. The metal silicide is selected from the group of Nb_5Si_3, V_5Si_3, Ta_5Si_3 and W_5Si_3.

IN THE CLAIMS:

On the first page of the claims, first line, change "Patent Claims" to:
--WHAT IS CLAIMED IS:--.

Please cancel original claims 1 to 27, without prejudice, and please add new claims 28 to 54 as follows:

--28. (New) A method for fabricating a composite material, the method comprising the steps of:

providing a parent substance containing a silicon nitride and a metal silicide, the silicon nitride being Si_3N_4 and the metal silicide being of a form Me_5Si_3, where Me is a metal;

establishing, as a function of a sintering temperature, an upper limit and a lower limit of partial nitrogen pressures so that the silicon nitride is stable at the lower limit and the metal silicide is stable at the upper limit; and

gas pressure sintering the parent substance in a nitrogenous atmosphere based on the lower limit and the upper limit.

29. (New) The method of claim 28, wherein the metal of the metal silicide is selected from a metal of one of a 5th subgroup and a 6th subgroup of the periodic table.

30. (New) The method of claim 29, wherein the metal of the metal silicide is selected from the group of Mo, Nb, V, Nb, Ta and W.

31. (New) The method of claim 28, wherein a weight ratio of Si_3N_4:Me_5Si_3 is between about 20:80 and about 80:20.

32. (New) The method of claim 28, wherein the parent substance includes sinter additives.

33. (New) The method of claim 32, wherein the sinter additives include at least one of aluminum oxide and yttrium oxide.

34. (New) The method of claim 32, wherein a concentration of the sinter additives in an initial mixture is retained at less than about 10 % by weight.

35. (New) The method of claim 28, wherein the parent substance includes pressing agents and binding agents.

36. (New) The method of claim 28, wherein the parent substance is ground into a powder.

37. (New) The method of claim 28, further comprising one of the following sets of steps:

(a) forming the parent substance into a desired shape by one of ceramic injection molding and cold-isostatic pressing before the step of gas pressure sintering; and

(b) (i) forming the parent substance into the desired shape by the one of the ceramic injection molding and the cold-isostatic pressing before the step of gas pressure sintering, and

(ii) forming the composite material by green processing subsequent to the step of gas pressure sintering.

38. (New) The method of claim 28, wherein the parent substance is cold-isostatically compressed at a pressure of between about 100 MPa and about 300 MPa.

39. (New) The method of claim 28, further comprising the step of pre-sintering the parent substance prior to the step of gas pressure sintering.

40. (New) The method of claim 39, wherein the step of pre-sintering is performed at a temperature of between about 500°C and about 700°C.

41. (New) The method of claim 39, wherein the step of pre-sintering is performed at a pressure of between about 0.05 MPa and about 0.2 MPa.

42. (New) The method of claim 28, wherein the step of gas pressure sintering is performed at a temperature of between about 1700°C and about 1900°C.

43. (New) The method of claim 28, wherein the step of gas pressure sintering is performed at a partial N_2 pressure of between about 0.5 MPa and about 1.0 MPa.

44. (New) The method of claim 29, wherein:

the metal of the metal silicide is molybdenum; and

the upper limit is set as an upper limit of partial N_2 pressures (p_{N2}) according to a first equation of $y_1 = 5.3071 \cdot \ln(T) - 37.014$, and

the lower limit is set as a lower limit of the partial N_2 pressures (p_{N2}) according to a second equation of $y_2 = 7.3494 \cdot \ln(T) - 54.124$,

where y_1 and y_2 represent $\lg(p_{N2}\ [\text{bar}])$ values.

45. (New) The method of claim 29, wherein:

the metal of the metal silicide is niobium; and

the upper limit is set as an upper limit of partial N_2 pressures (p_{N2}) according to a first equation of $y_1 = 7.8968 \cdot \ln(T) - 58.8$, and

the lower limit is set as a lower limit of the partial N_2 pressures (p_{N2}) according to a second equation of $y_2 = 8.2598 \cdot \ln(T) - 62.064$,

where y_1 and y_2 represent $\lg(p_{N2}\ [\text{bar}])$ values.

46. (New) The method of claim 28, wherein the step of gas pressure sintering is performed in a gas-pressure sintering furnace.

47. (New) A silicon-containing composite material comprising a silicon-containing material made of Si_3N_4 and a metal silicide, wherein the metal silicide is selected from the group of Nb_5Si_3, V_5Si_3, Ta_5Si_3 and W_5Si_3.

48. (New) The composite material of claim 47, wherein the metal silicide contains carbon.

49. (New) The composite material of claim 48, wherein the metal silicide contains carbon with a concentration specific to the composite material of about 0.3 % by weight to about 0.6 % by weight.

50. (New) The composite material of claim 47, wherein a mass ratio of Si_3N_4:Me_5Si_3 is between about 20:80 and about 80:20.

51. (New) The composite material of claim 47, wherein the parent substance includes sinter additives.

52. (New) The composite material of claim 51, wherein the sinter additives include at least one of aluminum oxide and yttrium oxide.

53. (New) The composite material of claim 51, wherein a concentration of the sinter additives in an initial mixture is less than about 10 % by weight.

54. (New) The composite material of claim 47, wherein the metal silicide is Nb_5Si_3.--.

Remarks

This Preliminary Amendment cancels, without prejudice, original claims 1 to 27 in the underlying PCT Application No. PCT/DE99/03155, and adds new claims 28 to 54. The new claims conform the claims to U.S. Patent and Trademark Office rules and do not add new matter to the application.

The above amendments to the specification and abstract are to conform the specification and abstract to U.S. Patent and Trademark Office rules or to correct informalities, and do not introduce new matter into the application.

The underlying PCT Application No. PCT/DE99/03155 includes an International Search Report, dated March 8, 2000. The Search Report includes a list of documents that were uncovered in the underlying PCT Application. A copy of the Search Report accompanies this Preliminary Amendment.

Applicants assert that the subject matter of the present application is new, non-obvious, and useful. Prompt consideration and allowance of the application are respectfully requested.

Respectfully Submitted,

KENYON & KENYON

Dated: 6/2/00

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METHOD FOR FABRICATING COMPOSITE MATERIALS AND REPRESENTATIVES OF SUCH COMPOSITE MATERIALS

Background of the Invention

The present invention relates to a method for fabricating a composite material out of a parent substance containing silicon nitride and a metal silicide, through gas pressure sintering in a nitrogenous atmosphere and a silicon-containing composite material, whose silicon-containing constituents are made of Si_3N_4 and of a metal silicide.

Composite materials, which contain silicon nitride and metal silicide, and methods for their preparation are generally known. The fabrication of such materials through single-axial hot-pressing (unconfined sintering under pressure) is described in German patents DE 37 34 274 C2 and DE 36 06 403 C2, the parent substance containing Si_3N_4 and, as silicide, $MoSi_2$, and in the EP 0 335 382 A1, the parent substance containing Si_3N_4, Mo_5Si_3 as silicide and carbon, and the fabricated material containing as metal silicide, Mo_5Si_3C or, more precisely, $Mo_{5-X}Si_3C_{1-Y}$ ($0 \leq X \leq 2$; $0 \leq Y \leq 1$). The electrical properties of the materials fabricated in this manner are able to be selectively adjusted. The method is industrial and requires considerable outlay for energy consumption. The application of the method only permits fabrication of complex geometrical structures in expensive, hard-machining operations.

German Patent DE 195 00 832 Al, i.e., European Patent EP 0 721 925 A2 discuss the fabrication of highly heat-resistant silicon nitride composite materials, which contain a reinforcement component of Me_5Si_3 and, moreover, $MeSi_2$ or $MeSi_2$, and silicides of other stoichiometries, Me standing for metal. Mixed into the parent substance as metal silicide are $MeSi_2$ and Me_5Si_3, or only $MeSi_2$. The metals are preferably selected from the group including molybdenum, tungsten, chromium, tantalum, niobium, manganese and vanadium. The sintering is performed as gas pressure sintering (at N_2 pressures of 100 bar), which makes it possible to fabricate molded articles (shaped bodies), virtually with their final contours, in ceramic injection molding or pressing processes, with subsequent green processing, or in hot-pressing (sintering under pressure) processes. Special electrical properties cannot be

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adjusted.

The Present Invention and Advantages Thereof

The object of the present invention is an industrially simple and energy-saving method for fabricating composite materials containing silicon nitride and metal silicide and having fixed electrical properties, which makes it possible to manufacture the molded articles, virtually with their final contours, from the composite material, prior to the sintering operation, and to specify representatives of such composite materials.

This objective is achieved by a method of the type mentioned at the outset, where Me_5Si_3 is introduced as the metal silicide into the parent substance, the partial pressure of the nitrogen being established as a function of the sintering temperature in such a way that, at the lower limit of the practical range, Si_3N_4 is still thermodynamically stable and, at the upper limit, Me_5Si_3, and is dissolved into a composite material of the type mentioned at the outset, the metal silicide being selected from the group Nb_5Si_3, V_5Si_3, Ta_5Si_3 and W_5Si_3.

The inventors discovered a way to exploit the advantages of the gas-pressure sintering method, at the same time while manufacturing composite materials having fixed electrical properties. They ascertained that the electrical properties cannot be adjusted in a determinate fashion (definably) when N_2 partial pressures are applied above a specific pressure range. During test trials, they found a range of the N_2 partial pressures within which one can prevent other silicon-containing components, besides Si_3N_4 and Me_5Si_3, from being present in the finished composite material. In this manner, they were able to fabricate composite materials having fixed electrical properties. In comparison to the hot-pressing (sintering under pressure) method, the gas-pressure sintering method makes do with a much simpler sintering device. Compact, high-strength materials are able to be fabricated with the method according to the present invention. In comparison to materials containing $MeSi_2$, materials containing Me_5Si_3 exhibit a very low temperature dependency of the electrical conductivity.

It is not critical when the method is carried out in such a way that the metal silicide in the composite material has a carbon concentration (preferably between about 0.3 and about 0.6 %

by weight specific to the composite material), i.e., is present as $Me_5Si_3(C)$.

Further advantageous refinements of the method according to the present invention and of the composite materials according to the present invention are delineated in the dependent claims.

Drawing

In the following, the present invention is elucidated on the basis of exemplary embodiments illustrated in the drawing, whose figures show:

Figure 1 plotted in a diagram over the sintering temperature, the logarithm of the lower and upper limit values of the N_2 partial pressures, applicable in the method according to the present invention, for fabricating a composite material containing Mo_5Si_3; and

Figure 2 the same as in Figure 1, however, for fabricating a composite material containing Nb_5Si_3.

The exemplary embodiments of the method according the present invention described in the following are, in fact, particularly advantageous. However, they are merely provided by way of example, and many variations are possible, without departing from the scope of the claims.

To fabricate the composite materials, a preconditioned Si_3N_4 powder is first mixed with sinter additives, such as Al_20_3, Y_20_3, or the like, which - in terms of the entire inorganic concentration -, make up less than about 10% by weight, Me_5Si_3 in suitable percentages by weight and, in some instances, organic pressing and/or binding agents, with the addition of an organic solvent - preferably - in an attritor mill. The attrited suspension is dried, for example, in a rotary evaporator. From the dried powder, through cold-isostatic pressing at pressures of between about 150 and 250 MPa, molded articles are produced, which, subsequent to the pressing operation, can obtain their final shape in a green processing. Other processing possibilities following the introduction of appropriate binding agents, include ceramic

injection molding (CIM) or extrusion. For debinding and/or presintering purposes, the molded articles are treated at approximately 600°C under a pressure of 1 bar in an inert gas atmosphere for about two hours, the organic constituents being removed, virtually without leaving any residues. The main sintering operation then follows, preferably in a gas-pressure sintering furnace at a temperature within a range of about 1700 and 1900°C, and preferably between about 1800 and 1900°C, under a defined partial N_2 pressure (total pressure between about 0.1 MPa and 10 MPa), which is set so as to achieve thermodynamic equilibrium of the Si_3N_4 phase and the Me_5Si_3 or $Me_5Si_3(C)$ phase during the sintering compression, i.e., to ensure they do not enter into any chemical reactions. The usable range of the partial N_2 pressure at a specific temperature is dependent upon the metal silicide. In the diagrams of Figures 1 and 2, the ranges of the usable partial N_2 pressures, measured in bar, (p_{N2}) for mixtures containing Mo_5Si_3 or Nb_5Si_3 are plotted as log(p_{N2} [bar]) as a function of the temperature. In each case, the upper and lower limiting curves satisfy, for Mo-containing mixtures, the equations

$$y_1 = 5.3071 \cdot \ln(T) - 37.014$$

respectively

$$y_2 = 7.3494 \cdot \ln(T) - 54.124$$

and, for Nb-containing mixtures, the equations

$$y_1 = 7.8968 \cdot \ln(T) - 58.8$$

respectively

$$y_2 = 8.2598 \cdot \ln(T) - 62.064,$$

y_1 and y_2 representing lg(p_{N2} [bar]) values. Below the limited range, Si_3N_4 reacts with Me_5Si_3. Above the limited range, Me_5Si_3 reacts with nitrogen. The curves were determined in serial investigations, in that, at a fixed temperature of between about 1700 and 1900°C, the partial N_2 pressures were determined at which Me_5Si_3 and Si_3N_4 are thermodynamically stable. The criterion that no reaction took place is, in each case, that only the desired silicon-containing phases are found in the X-ray diffractogram of the sintered material. The equations named above were then determined on the basis of these values, of known data, such as enthalpies of formation, and of thermodynamic functions. The sintering process takes about two to five hours.

The specific electrical resistance of the composite materials fabricated in accordance with the present invention is adjusted through the selection of the metal in the silicide and the concentration and the distribution of the silicide in the composite material. Beyond the particular percolation range, specific electrical resistances of between about $1.7 \cdot 10^{-4} \Omega cm$ and $1 \cdot 10^{12} \Omega cm$ can be reproducibly adjusted with materials containing $Nb_5Si_3(C)$, and of between about $1 \cdot 10^{-5} \Omega cm$ and $1 \cdot 10^{12} \Omega cm$ with materials containing $Mo_5Si_3(C)$. The specific resistance is measured using the four-point method.

Using qualitative and quantitative chemical and physico-chemical analyses and radiographic phase analysis, one can verify that - apart from the carbon concentration and without consideration of the organic constituents - the sintered materials have the same composition as the mixture that the fabrication process originated with. During the sintering process in a graphite furnace, the carbon is preferably contained in the metal silicide with a concentration, in terms of the composite material, of between about 0.3 and 0.6 % by weight, and quite preferably with about 0.5 % by weight. The room (ambient) temperature stabilities of the composite materials do not lie under 500 MPa.

Besides standing for niobium and molybdenum having comparable results for all metals of the 5th and 6th subgroup of the periodic system, Me can stand, in particular, for vanadium, tantalum, chromium and tungsten.

The method of the present invention is described in greater detail in the following on the basis of two special examples.

Example 1

The parent substance was mixed from 36 % by weight of Si_3N_4, 1.7 % by weight of Al_2O_3, 2.38 % by weight of Y_2O_3, 60 Nb_5Si_3 % by weight and the usual pressing and/or binding agents. The average particle size of the Si_3N_4 was 0.7 μm, and that of the Nb_5Si_3 0.7 μm. The cold isostatic compression at 200 MPa was followed by a pre-sintering under an inert gas at up to 600°C, argon being used (nitrogen also could have been used). Sintering subsequently took place at a partial N_2 pressure of 0.5 MPa (total pressure 1 MPa) and 1800°C in a

graphite furnace.

The density of the composite material obtained was 97% of the material density. The radiographic phase analysis performed after the sintering process yielded exclusively Si_3N_4 and $Nb_5Si_3(C)$ as silicon-containing phases. As a specific electrical resistance, $3{\cdot}6{\cdot}10^{-3}\Omega cm$ was determined at 25 °C. The temperature coefficient of the specific electrical resistance amounted to $2{\cdot}10^{-4}\ K^{-1}$.

Example 2

Besides that the inorganic constituents of the parent substance were made up of 54 % by weight of Si_3N_4, 2.6 % by weight of Al_2O_3, 3.4 % by weight of Y_2O_3, 40 Nb_5Si_3 % by weight, the method was carried out in the same manner as in Example 1.

The analyses performed on the sintered material likewise yielded the attained material density amount of 97%, the radiographic phase analysis yielded exclusively Si_3N_4 and $Nb_5Si_3(C)$ as silicon-containing phases, and $2{\cdot}10^{2}\Omega cm$ at 25 °C was determined as a specific electrical resistance.

Patent Claims

1. A method for fabricating a composite material out of a parent substance containing silicon nitride and metal silicide, through gas pressure sintering in a nitrogenous atmosphere, characterized in that, as metal silicide, Me_5Si_3 is introduced into the parent substance, the partial nitrogen pressure is established as a function of the sintering temperature in such a way that, still stable at the lower limit of the practical range is Si_3N_4 and, at the upper limit, Me_5Si_3.

2. The method as recited in Claim 1, characterized in that the metal in the silicide is selected from a metal of the 5th or 6th subgroup.

3. The method as recited in Claim 2, characterized in that the metal is selected from the group Mo, Nb, V, Nb, Ta and W.

4. The method as recited in one of Claims 1 through 3, characterized in that a weight ratio of between about 20:80 and 80:20 is adjusted for Si_3N_4:Me_5Si_3.

5. The method as recited in one of Claims 1 through 4, characterized in that sinter additives are added to the parent substance.

6. The method as recited in Claim 5, characterized in that aluminum oxide and/or yttrium oxide and/or similarly acting materials are added as sinter additives.

7. The method as recited in Claim 5 or 6, characterized in that the concentration of sinter additives in the initial mixture is retained at < about 10 % by weight.

8. The method as recited in one of Claims 1 through 7, characterized in that pressing and/or binding agents are added to the parent substance.

9. The method as recited in one of Claims 1 through 8, characterized in that the parent substance is ground.

10. The method as recited in one of Claims 1 through 9, characterized in that the parent substance is formed in a desired shape through ceramic injection molding or cold-isostatic pressing, and, if indicated, through subsequent green processing.

11. The method as recited in one of Claims 1 through 10, characterized in that the parent substance is densified cold-isostatically at a pressure of between about 100 and 300 MPa.

12. The method as recited in one of Claims 1 through 11, characterized in that prior to the sintering operation, the parent substance is subjected to a pre-sintering.

13. The method as recited in Claim 12, characterized in that the presintering takes place at a temperature of between about 500 and 700°C.

14. The method as recited in Claim 12 or 13, characterized in that the presintering takes place at a pressure of between about 0.05 and 0.2 MPa.

15. The method as recited in one of the Claims 1 through 14, characterized in that the sintering is carried out between about 1700 and 1900°C.

16. The method as recited in one of the Claims 1 through 15, characterized in that the sintering is carried out at a partial N_2 pressure of between about 0.5 and 1.0 MPa.

17. The method as recited in one of the Claims 2 through 16, characterized in that molybdenum is used as metal, and that, as a function of the temperature, the upper limit of the partial N_2 pressures (p_{N2}) is set in accordance with the equation $y_1 = 5.3071 \cdot \ln(T) - 37.014$ and the lower limit in accordance with the equation $y_2 = 7.3494 \cdot \ln(T) - 54.124$, y_1 and y_2 representing $\lg(p_{N2}\ [\text{bar}])$ values.

18. The method as recited in one of the Claims 2 through 15, characterized in that niobium is used as metal, and that, as a function of the temperature, the upper limit of the partial N_2 pressure (p_{N2}) is set in accordance with the equation $y_1 = 7.8968 \cdot \ln(T) - 58.8$ and the lower limit in accordance with the equation $y_2 = 8.2598 \cdot \ln(T) - 62.064$, y_1 and y_2

representing $\lg(p_{N2}\ [\mathrm{bar}])$ values.

19. The method as recited in one of the Claims 1 through 18, characterized in that the sintering is carried out in a gas-pressure sintering furnace.

20. A silicon-containing composite material, whose silicon-containing constituents are made of Si_3N_4 and of a metal silicide, characterized in that the metal silicide is selected from the group Nb_5Si_3, V_5Si_3, Ta_5Si_3 and W_5Si_3.

21. The composite material as recited in Claim 20, characterized in that the metal silicide contains carbon.

22. The composite material as recited in Claim 21, characterized in that the metal silicide contains carbon with a concentration specific to the composite material of about 0.3 to about 0.6 % by weight.

23. The composite material as recited in one of Claims 20 through 22, characterized in that the mass ratio of Si_3N_4:Me_5Si_3 is between about 20:80 and 80:20.

24. The composite material as recited in one of Claims 20 through 23, characterized in that sinter additives are added to the parent substance.

25. The composite material as recited in Claim 24, characterized in that the sinter additives are made of aluminum oxide and/or yttrium oxide and/or similarly acting materials.

26. The composite material as recited in Claim 24 or 25, characterized in that the concentration of sinter additives in the initial mixture is < about 10 % by weight.

27. The composite material as recited in one of Claims 20 through 26, characterized in that the metal silicide is Nb_5Si_3.

Abstract

To manufacture composite materials containing silicon nitride and metal silicide and having fixed electrical properties, in an industrially simple and energy-saving fashion, the aim being to produce the molded articles, virtually with their final contours, from the composite materials, prior to the sintering operation, and to specify representatives of such composite materials, a method is proposed where a parent substance containing Si_3N_4 and metal silicide is subjected to the gas pressure sintering in a nitrogenous atmosphere, where, as metal silicide, Me_5Si_3 is introduced into the parent substance, where the partial nitrogen pressure is established as a function of the sintering temperature in such a way that, still stable at the lower limit of the practical range is Si_3N_4 and, at the upper limit, Me_5Si_3 and a silicon-containing composite material, whose silicon-containing constituent is made of Si_3N_4 and of a metal silicide, the metal silicide being selected from the group Nb_5Si_3, V_5Si_3, Ta_5Si_3 and W_5Si_3.

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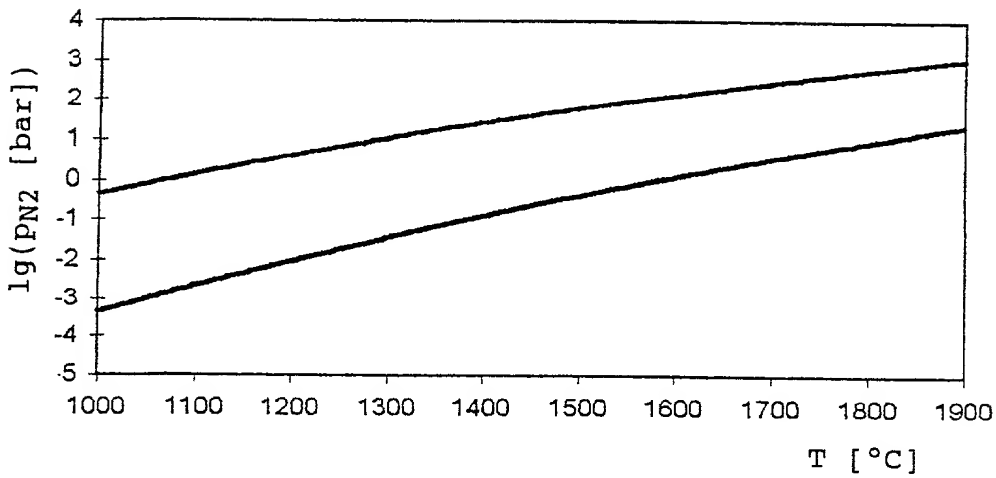
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Fig. 1

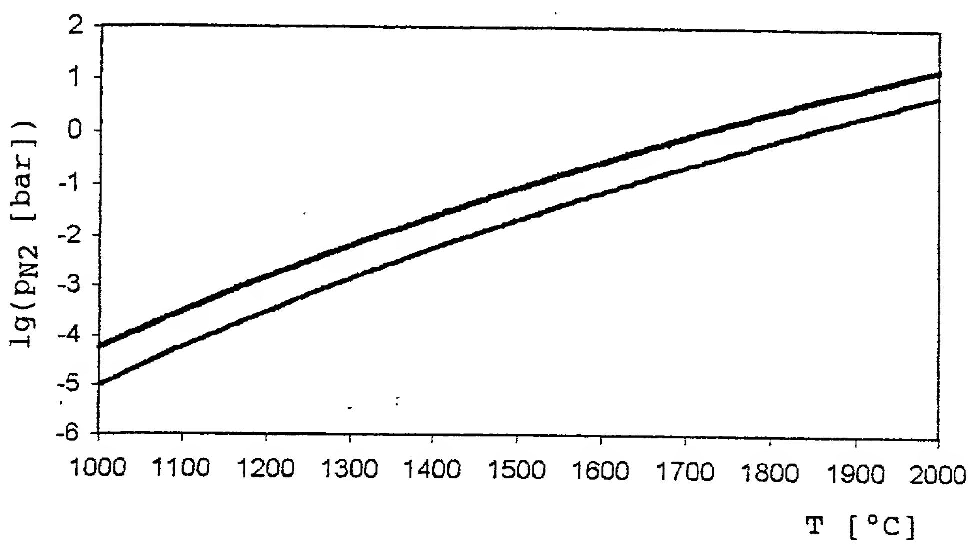
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Fig. 2

[10191/1438]

DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled **METHOD FOR FABRICATING COMPOSITE MATERIALS AND REPRESENTATIVES OF SUCH COMPOSITE MATERIALS**, the specification of which was filed as PCT International Application No. **PCT/DE99/03155** on October 1, 1999 and as U.S. Application Serial No. 09/555,777.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, § 1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, § 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application(s) for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

PRIOR FOREIGN APPLICATION(S)

Number	Country filed	Day/month/year	Priority Claimed Under 35 USC 119
198 45 532.1	Fed. Rep. of Germany	2 October 1998	Yes

(2) And I hereby appoint Richard L. Mayer (Reg. No. 22,490) and Gerard A. Messina (Reg. No. 35,952) my attorneys with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful and false statements may jeopardize the validity of the application or any patent issued thereon.

1-00

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